Quality Assurance Project Plan for

Analysis of Fish Fillet Samples for the Fish Plug Evaluation Study

Revision 1.0

June 6, 2018

Prepared for:

United States Environmental Protection Agency
Office of Water
Office of Science and Technology
Standards and Health Protection Division

Prepared by:

[redacted]

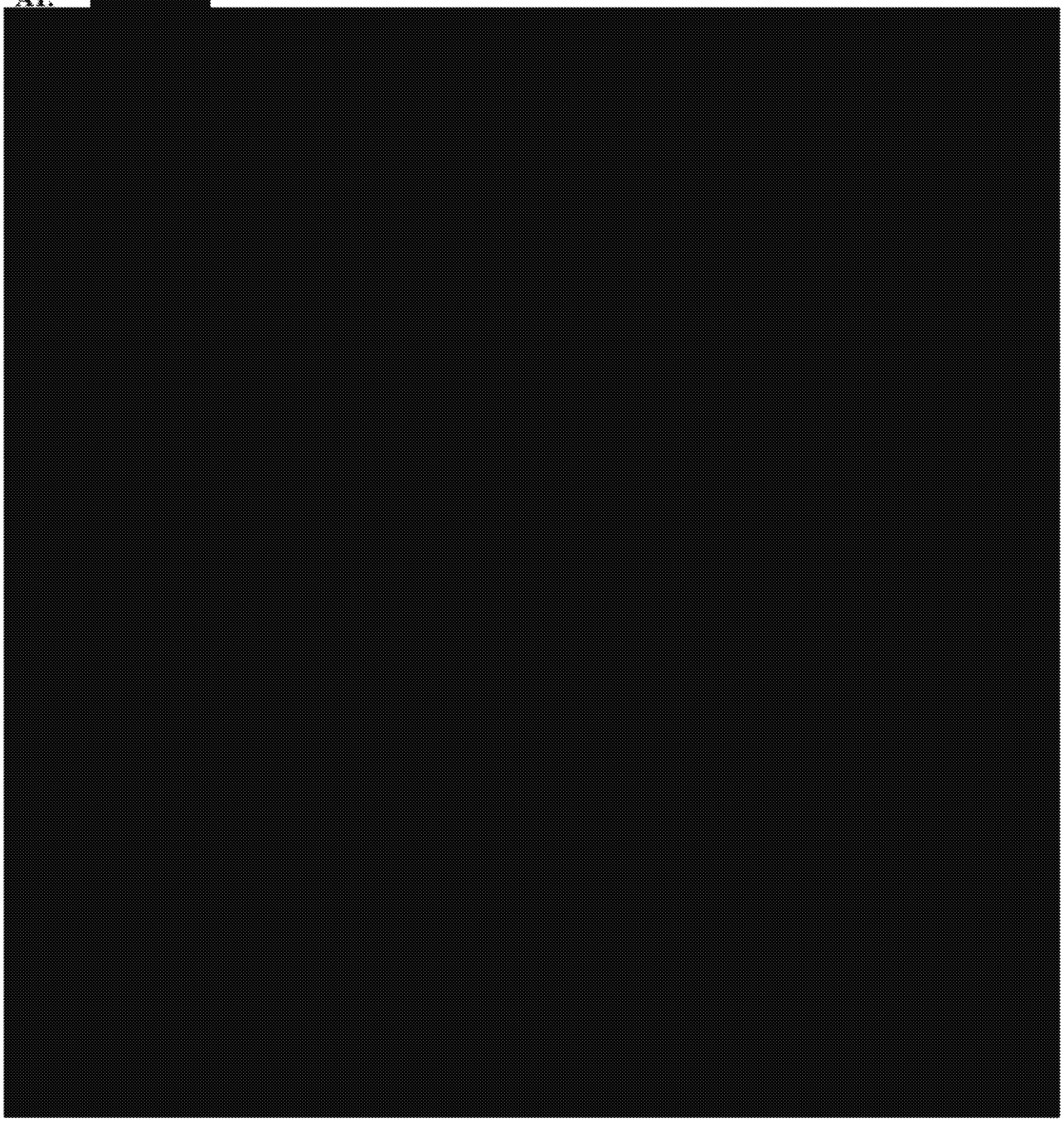
Analysis of Fish Fillet Samples for the Fish Plug Evaluation Study

A. PROJECT MANAGEMENT

This Quality Assurance Project Plan (QAPP) presents performance criteria, acceptance criteria, and objectives for the analysis of fish fillet plug and homogenized fillet tissue samples, as part of the Fish Plug Evaluation Study being conducted by the Office of Science and Technology (OST) within the U.S. Environmental Protection Agency's (EPA's) Office of Water (OW). The scope of the initial QAPP was limited to the analysis of fillet plug and homogenized fillet samples for mercury. This revision of the QAPP adds procedures and requirements for the analysis of fillet plug samples and homogenized fillet samples for selenium and percent solids. Details of the fish sample collection and preparation procedures are not described in this QAPP, but can be found in the Quality Assurance Project Plan for Fish Plug Evaluation Study Sample Collection and Preparation (USEPA 2018).

This QAPP was prepared in accordance with the most recent version of EPA QA/R-5, *EPA Requirements for Quality Assurance Project Plans* (USEPA 2001a), that was reissued in 2006. In accordance with EPA QA/R-5, this QAPP is a dynamic document that is subject to change as analytical activities progress. Changes to procedures in this QAPP must be reviewed by the Fish Plug Evaluation Study EPA Project Manager and the EPA Standards and Health Protection Division (SHPD) Quality Assurance Coordinator to determine whether the changes will impact the technical and quality objectives of the project. If so, the QAPP will be revised accordingly, circulated for approval, and forwarded to all project participants listed in the QAPP distribution list (Section A3). Key project personnel and their roles and responsibilities are discussed in the QAPP section to follow (Section A4), and project background information and a summary description of the project are provided in Sections A5 and A6, respectively.

A1. [redacted]



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List of Acronyms and Abbreviations

EPA	Environmental Protection Agency (also known as USEPA)
FPES	Fish Plug Evaluation Study
ID	Identification
LCS	Laboratory control sample
MDL	Method detection limit
ML	Minimum level
MS	Matrix spike
MSD	Matrix spike duplicate
OPR	Ongoing precision and recovery
OST	Office of Science and Technology
OW	Office of Water
OWOW	Office of Wetlands, Oceans, and Watersheds
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
QSA	Quality system audit
RSD	Relative Standard Deviation
SHPD	Standards and Health Protection Division
SOP	Standard operating procedure
SOW	Statement of work
WQC	Water quality criterion
WSD	Water Security Division within EPA's Office of Water

A3. Distribution List

A4. Project/Task Organization

The project team for Fish Plug Evaluation Study fish fillet tissue sample analysis consists of the EPA Project Manager in OST/SHPD, the EPA QA Officer in OST, the EPA QA Coordinator in OST/SHPD, the CSRA Project Leaders, and CSRA QA Officer who collectively provide scientific, technical, logistical, and quality control support for the study. The project team organization provides the framework for conducting fish sample analysis to meet study objectives. The organizational structure and function also facilitate project performance and adherence to QC procedures and QA requirements. The project organizational chart is presented in Figure 1. It identifies individuals serving in key roles for fish sample analysis and the relationships and lines of communication among these project team members. Responsibilities for key members of the project team are described below.

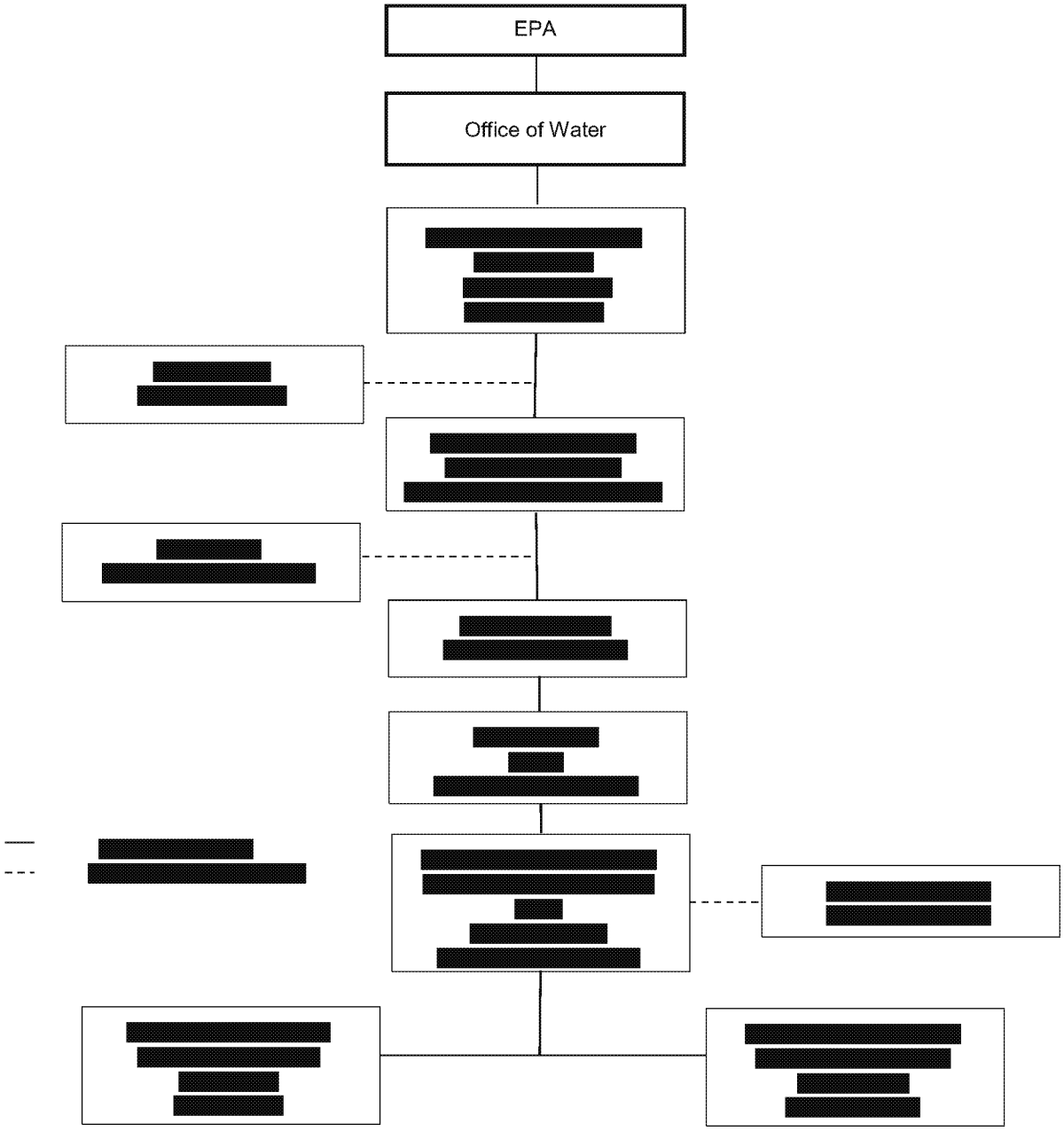

Figure 1. Fish Plug Evaluation Study (FPES) project team organization for sample analysis

[redacted] **EPA Project Manager** who is providing overall direction for planning and implementation of this study. This role involves the following responsibilities related to the Fish Plug Evaluation Study:

- coordinating with project team members to plan the study design
- directing development of this QAPP for fish sample collection and subsequent QAPP revisions for fish sample preparation
- reviewing and approving the Fish Plug Evaluation Study sample collection procedures and related field sampling materials, including training materials
- providing technical oversight for developing and implementing the fish sample preparation procedures and technical support for reviewing fish sample preparation QA/QC data
- managing analysis of fish fillet samples (plug and homogenized fillet samples) for target chemicals (mercury and selenium), which includes obtaining technical support for chemical analysis of fillet tissue samples, directing development of a sample analysis QAPP, providing for QA/QC review of the analytical results, developing the data files for statistical analysis of the data, reviewing and approving the final analytical QA report, and providing oversight for development of the database to store Fish Plug Evaluation Study plug and homogenized fillet results
- facilitating communication among project team members and coordinating with all of these individuals to ensure technical quality and adherence to QA/QC requirements
- developing and managing work assignments under OST or other EPA contracts to provide technical and logistical support for the Fish Plug Evaluation Study, providing oversight of all contractor activities, and reviewing and approving study deliverables for each work assignment
- scheduling and leading meetings and conference calls with project team members for planning study activities, reporting progress on study tasks, and discussing and resolving technical or other issues related to the study
- working with QA staff to identify corrective actions necessary to ensure that study quality objectives are met
- managing the development of and/or reviewing and approving all major work products associated with the Fish Plug Evaluation Study
- leading the process for planning and conducting statistical analysis of the Fish Plug Evaluation Study data
- collaborating with the project team for reporting the study results in technical journal articles and federal technical reports
- preparing presentations related to the Fish Plug Evaluation Study and presenting them in various forums (e.g., scientific conferences, government meetings, and webinars)

[redacted] **OST Quality Assurance Officer** who is responsible for reviewing and approving all Quality Assurance Project Plans (QAPPs) that involve scientific work being conducted by OST. [redacted] **Standards and Health Protection Division QA Coordinator** who is responsible for reviewing and recommending approval of all QAPPs that

include scientific work being conducted by the Standards and Health Protection Division (SHPD) within OST. The OST QA Officer and SHPD QA Coordinator are also responsible for the following QA/QC activities:

- reviewing and approving this QAPP
- reviewing and evaluating the QA/QC requirements and data for all the Fish Plug Evaluation Study activities and procedures
- conducting external performance and system audits of the procedures applied for all Fish Plug Evaluation Study activities
- participating in Agency QA reviews of the study

[redacted] who is responsible for managing all aspects of the technical support being provided by CSRA staff for the Fish Plug Evaluation Study. Her specific responsibilities include the following:

- monitoring the performance of CSRA staff participating in this study to ensure that they are following all QA procedures described in this QAPP that are related to CSRA tasks being performed to support this study
- ensuring completion of high-quality deliverables within established budgets and time schedules
- participating in meetings and conference calls with project team members for planning study activities, reporting progress on study tasks, and discussing and resolving technical issues related to the study

[redacted]e **CSRA Project Leader** who is providing technical support for the Fish Plug Evaluation Study. His specific responsibilities include the following:

- providing direct technical support for the following Fish Plug Evaluation Study activities:
  - preparing information related to technical and quality assurance requirements for chemical analysis of fish fillet plug and homogenized fillet tissue samples for mercury and selenium, verification and validation of analytical data, and development of Fish Plug Evaluation Study documents (including this QAPP)
  - obtaining subcontractor laboratory services to analyze fish plug and fillet tissue samples for mercury and selenium, and providing technical and QA oversight of laboratory operations
  - completing analytical data review and developing the analytical data QA report
  - preparing analytical data files for statistical analysis and public release
  - developing and maintaining a project database for storing Fish Plug Evaluation Study field and analytical data, and initiating queries of the database to respond to data requests from Agency and external users
  - obtaining freezer space that meets the requirements for long-term storage of archived fish tissue samples, organizing the archived fish tissue samples by project to facilitate retrieval of the samples, and developing and maintaining an inventory of the archived samples, as required

  - preparing summary project information and graphics for development of project fact sheets, presentations, and other EPA meeting and outreach materials
  - supporting development of technical journal articles and final project reports
- participating in meetings and conference calls with project team members for planning study activities, reporting progress on study tasks, and discussing and resolving technical issues related to the study

[redacted] **CSRA QA Officer** whose primary responsibilities include the following:

- assisting CSRA's Work Assignment Lead and Project Leader with the development and review of this QAPP
- approving this QAPP
- providing oversight for the implementation of QA procedures related to CSRA tasks that are described in this QAPP
- reporting deviations from this QAPP to the CSRA Work Assignment Lead and Project Leader and recommending corrective actions to resolve these deviations

A5. Problem Definition/Background

In 2013, EPA's Office of Wetlands, Oceans, and Watersheds (OWOW) within OW initiated fish plug sampling from whole fish collected at 361 river sites for the 2013-14 National Rivers and Streams Assessment (NRSA) human health fish tissue indicator. Collecting and analyzing fillet plug samples was applied as a more cost-effective alternative to obtain mercury data for human health applications than the routine approach of removing entire fillets from each fish in a sample and homogenizing the fillet tissue for mercury analysis. OWOW expanded use of fish fillet plug sampling for mercury analysis during the 2015 National Coastal Condition Assessment (NCCA) by applying this fish tissue sampling technique on fish samples collected from the 225 Great Lakes sites and the 684 marine sites along the coasts of the contiguous United States that were designated for fish sampling.

Prior to these EPA surveys, a few states were experimenting with fish plug sampling to monitor mercury contamination in fish. EPA's widespread use of fish plug sampling in these two recent National Aquatic Resource Surveys has prompted more states to introduce this sampling technique into their fish monitoring programs. However, the question remains about whether fish fillet plug sampling and analysis can serve as a reliable surrogate for the traditional approach of homogenizing and analyzing whole fillet tissue to monitor mercury concentrations in fish. Additionally, this study will investigate if it is technically feasible to apply fillet plug sampling and analysis to monitor selenium concentrations in fish below the recently released water quality criterion (WQC) for selenium in fish tissue of 11,300 ng/g dry weight (USEPA 2016)

A6. Project/Task Description

OST is conducting the Fish Plug Evaluation Study to address the fundamental question about comparability of fillet concentration results when analyzing fish fillet plug samples vs. homogenized whole fillet tissue samples for mercury and selenium. Data from this study should allow EPA to determine if fish fillet plug sampling and analysis can be applied as a technically comparable alternative to homogenizing and analyzing whole fillet tissue samples for these two

metals. Depending on the outcome of the study, there could be important cost implications if study data demonstrate that fish fillet plug analysis can serve as a reliable alternative for monitoring levels of mercury and selenium in fish. A positive outcome for the study would be to identify fish fillet plug sampling and analysis as an effective approach that state and federal agencies can use for surveillance and compliance monitoring of mercury and selenium levels in fish at much lower costs.

The design of the Fish Plug Evaluation Study allows for conducting the study in two phases: the mercury phase and the selenium phase. EPA began implementing the mercury phase of the study in June 2017 and initiated the selenium phase in May 2018. Fish sampling for the Fish Plug Evaluation Study is being conducted in two waterbody types: the Great Lakes and mid-Atlantic rivers. Three target species consisting of lake trout, walleye, and Chinook salmon are being collected from three Great Lakes. Three additional target species (i.e., largemouth bass, smallmouth bass, and blue catfish) are being collected from three mid-Atlantic rivers (refer to Section B1 for more study design details).

Mercury Phase

The mercury phase involves collecting and analyzing a greater number of fillet tissue samples (900 samples) to thoroughly test the comparability of results from analysis of the following three types of fillet samples for mercury: field-extracted fillet plug samples, lab-extracted fillet plug samples, and homogenized whole fillet tissue samples. Ten individual fish of each of the six target species (a total of 60 fish) and five field-extracted fillet plug samples from each whole fish sample (a total of 300 plug samples) were collected for the mercury phase of the study during August and September 2017. The remaining 600 fillet samples for the mercury phase of the study consist of 300 lab-extracted fillet plug samples and 300 homogenized whole fillet samples (five replicates per whole fish for each type of fillet sample).

Selenium Phase

The selenium phase of the study builds on the results from the mercury phase and involves analysis of a smaller number (360 samples) of the same three types of fillet samples for selenium: field-extracted fillet plug samples, lab-extracted fillet plug samples, and homogenized whole fillet tissue samples. Five individual fish of each of the six target species (a total of 30 fish) and four field-extracted fillet plug samples from each whole fish sample (a total of 120 plug samples) are being collected for the selenium phase of the study. The remaining 240 fillet samples for the selenium phase of the study consist of 120 lab-extracted fillet plug samples and 120 homogenized whole fillet samples (four replicates per whole fish for each type of fillet sample). The selenium phase also provides the opportunity to determine if using small tissue volumes is technically feasible to monitor selenium levels in fish below the WQC of 11,300 ng/g on a dry-weight basis.

Note: In contrast to mercury, which can be measured at very low levels (sub parts per billion) in fish tissue, readily available analytical methods for selenium in fish tissue are much less sensitive and sample size will be a limiting factor for this study. Therefore, the focus of the selenium phase is not on "how low you can go," but whether or not measurements can be made at or below the WQC using fillet plug samples.

A7. Quality Objectives and Criteria

The overall quality objective for the analysis of the Fish Plug Evaluation Study fish fillet plug and homogenized fillet tissue samples is to obtain complete sets of mercury data and selenium data and to produce data of known and documented quality. Completeness is defined as the percentage of samples collected in the study for which usable analytical results were produced. The goal for completeness is 95%.

The method and quality control acceptance criteria employed by the commercial analytical laboratories for analyses of the Fish Plug Evaluation Study fish fillet plug and homogenized fillet tissue samples for mercury and selenium are summarized in Section B.5. Data usability for each analysis will be assessed using QC criteria established by the respective analytical methods.

A8. Special Training/Certification

All laboratory staff involved in the analysis of fish fillet plug and homogenized fillet tissue samples must be proficient in the associated tasks, as required by the analytical laboratory's existing quality system. All contractor staff involved in analytical data review and assessment will be proficient in data review, and no specialized training is required for data reviewers for this project.

A9. Documents and Records

The Statements of Work (SOWs) for the analytical subcontracts will provide the specific requirements for laboratory deliverables. The major points are summarized below:

- The laboratory must provide reports of all results required from analyses of environmental and QC samples.
- Summary level data must be submitted in electronic format and must include the following information: EPA sample number, analyte name and Chemical Abstract Service number, laboratory sample ID, measured amount, reporting units, sample preparation date, and analytical batch ID (if applicable).
- The laboratory shall provide raw data in the form of direct instrument readouts with each data package. Raw data include:
  - Copy of traffic report, chain-of-custody records, or other shipping information
  - Instrument readouts and quantitation reports for analysis of each sample, blank, standard and QC sample, and all manual worksheets pertaining to sample or QC data or the calculations thereof
  - Copies of bench notes, including those documenting the preparation of standards and the instrumental analyses

The laboratories will maintain records and documentation associated with these analyses for a minimum of five years after completion of the study. Additional copies will be maintained by CSRA for the time period established under the terms of EPA Contract No. EP-C-15-012, and will be transferred to EPA on request.

B. DATA GENERATION AND ACQUISITION

B1. Sampling Process Design (Experimental Design)

The Fish Plug Evaluation Study is designed to assess the comparability of mercury concentrations in fish fillet plugs vs. homogenized whole fillet tissue samples and to test the feasibility and applicability of fish fillet plug sampling and analysis for conducting compliance monitoring associated with EPA's fish tissue-based selenium water quality criterion. Following are the key elements of the Fish Plug Evaluation Study design:

- Fish sampling is being conducted in two waterbody types, the Great Lakes and U.S. rivers in the mid-Atlantic region. Lake Erie, Lake Michigan, and Lake Ontario are being targeted for Great Lakes fish sample collection, and the Anacostia River, the Potomac River, and the St. Lawrence River are being targeted for river fish collection.
- Individual whole fish samples are being collected from each waterbody type to provide plug and homogenized fillet tissue samples for mercury and selenium analyses.
- To provide tissue samples for mercury analysis, 10 specimens of three species each were collected from the designated Great Lakes and from the designated rivers. Target species for the Great Lakes are lake trout, walleye, and Chinook salmon. Target species for the rivers are largemouth bass, smallmouth bass, and blue catfish. This fish sampling effort, which was completed in September 2017, yielded 60 individual whole fish samples to be prepared for mercury analysis.
- Five replicates each of three types of fish tissue samples are prepared from each fish for mercury analysis (see Figure 2): field-extracted fillet plug samples, lab-extracted fillet plug samples, and lab-prepared homogenized whole fillet tissue samples, yielding 900 fish fillet tissue samples for mercury analysis (60 fish x 3 fillet sample types per fish x 5 replicates per fillet sample type = 900 fish fillet tissue samples).

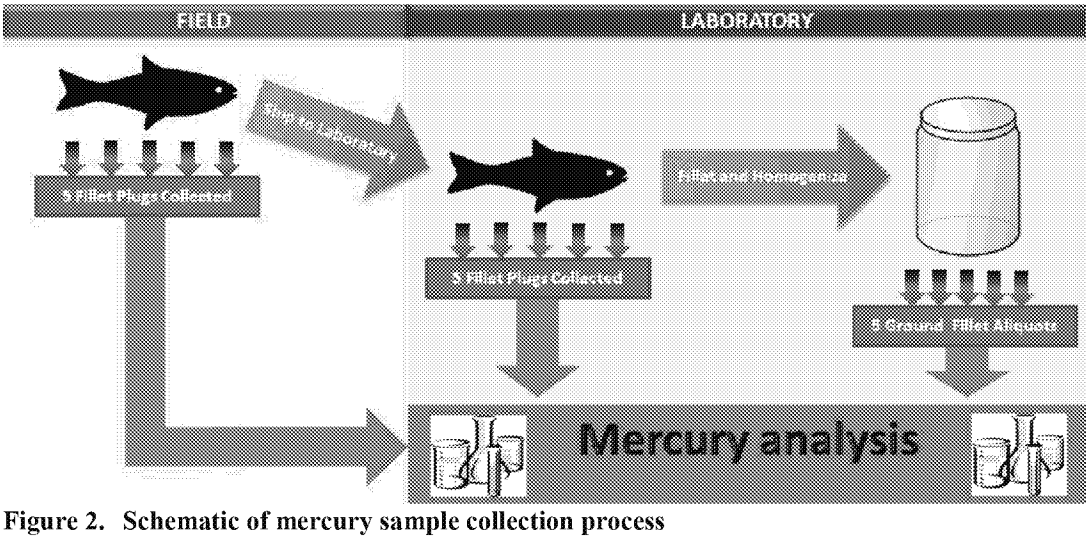

Figure 2. Schematic of mercury sample collection process

- To provide tissue samples for selenium analysis, 5 specimens of three species each are collected from the designated Great Lakes and from the designated rivers. Target species for the Great Lakes and rivers are the same as for mercury analysis (i.e., lake trout, walleye, and Chinook salmon for the Great Lakes and largemouth bass, smallmouth bass,

and blue catfish for the rivers). This fish sampling effort will yield 30 individual whole fish samples to be prepared for selenium analysis.

- Four replicates each of three types of fish fillet samples will be prepared from each fish for selenium analysis (see Figure 3): field-extracted fillet plug samples, lab-extracted fillet plugs, and lab-prepared homogenized whole fillet tissue samples, yielding 360 fish fillet tissue samples for selenium analysis (30 fish x 3 fillet sample types per fish x 4 replicates per fillet sample type = 360 fish fillet tissue samples).

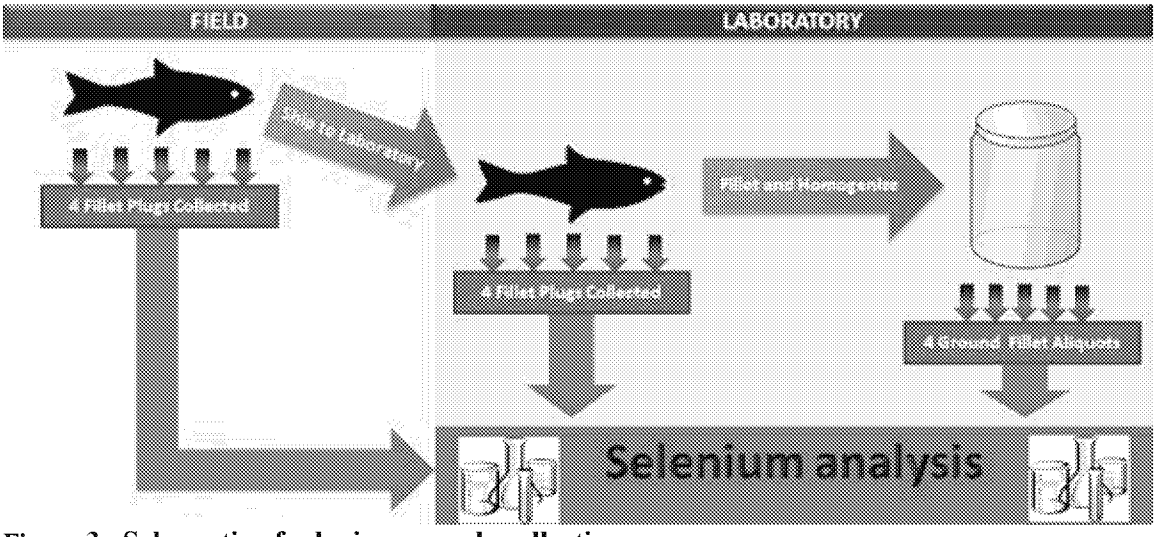

Figure 3. Schematic of selenium sample collection process

- Whole fish and field-extracted fillet plug samples are hand-delivered to the Tetra Tech laboratory in Owings Mills, MD, for interim storage and fish sample preparation. The 60 whole fish samples and 300 field-extracted plug samples collected for the mercury phase of the study during August and September 2017 were stored in freezers at the Tetra Tech laboratory prior to initiation of fish tissue sample preparation and/or sample analysis. The 30 whole fish samples and 120 field-extracted plug samples collected for the selenium phase of the study are scheduled for collection in June and July 2018. They will be stored in freezers at the Tetra Tech laboratory prior to initiation of fish tissue sample preparation and/or sample analysis.

- The designated type and number of fillet tissue samples will be analyzed for mercury and selenium as noted above for the two phases of the study. In addition, homogenized whole fillet tissue samples from each of the 90 fish collected for the study (60 fish during the mercury phase and 30 fish during the selenium phase) will be analyzed for lipids during the fish sample preparation process. All of the fillet tissue samples (field-extracted plugs, lab-extracted plugs, and homogenized whole fillet tissue samples) from each of the 30 fish collected for the selenium phase of the study will also be analyzed for percent solids in order to provide selenium results on the dry-weight basis specified in the WQC. To provide tissue mass for the solids measurements, an additional 4 field-extracted plugs and 4 lab-extracted plugs will be collected beyond those illustrated in Figure 3 for the selenium analysis itself. These additional plug samples will be collected as single plugs and will provide data on the variability of the solids content of the fish tissues, independent of the variability of the selenium content.

B2. Sample Collection and Preparation Methods

Procedures and requirements for collection of Fish Plug Evaluation Study whole fish and field-extracted fillet plug samples and for preparation of fillet tissue samples are detailed in Revision 2 of the Fish Plug Evaluation Study Sample Collection and Preparation QAPP (USEPA 2018) and are beyond the scope of this analytical QAPP.

B3. Sample Handling and Custody

This section describes the sample handling and custody procedures that apply to the shipment of the fish fillet plug and homogenized fillet tissue samples to the analytical laboratories selected for analysis of tissue samples for mercury and for selenium and percent solids.

In coordination with CSRA, Tetra Tech staff will initiate packing and shipping the fish fillet plug and homogenized fillet tissue samples from their fish sample preparation laboratory in Owings Mills, MD, to the respective analytical laboratories designated for mercury and selenium analyses of the study fillet tissue samples following procedures described in Revision 2 of the Fish Plug Evaluation Study Sample Collection and Preparation QAPP (USEPA 2018). The CSRA Project Leader provides a template for sample tracking paperwork that is completed by Tetra Tech staff and included in each shipment, notifies the laboratory in advance of each shipment, tracks the progress of each shipment, and identifies and resolves any delays that arise during shipment of the tissue samples.

When received at the analytical laboratory, the fish fillet plug and homogenized fillet tissue samples are inspected for damage, logged into the laboratory, and immediately placed into freezers. Because the samples are shipped frozen, typical temperature blanks consisting of a bottle of water are not practical (they may break due to expansion), so they are not required. The laboratory measures and records the temperature of the coolers containing the samples on receipt using an infrared temperature sensor or other suitable device. The CSRA Project Leader is notified of the receipt of the fish plug and fillet tissue samples by email, and will advise OST of tissue sample receipt on the day of delivery. Any questions from the analytical laboratory regarding sample paperwork or condition will be sent to CSRA, routed to OST or Tetra Tech, as appropriate, and CSRA will send the answers back to the laboratory.

Fish fillet plug and homogenized fillet tissue samples will be stored frozen at $\leq$ -20°C until analyzed. There are concerns that the small tissue plug samples may become dehydrated during prolonged frozen storage, so the mercury and selenium analysis laboratories are required to hold the plug samples in the freezer no longer than 60 days before beginning analysis of the samples. To ensure timely analysis of the plug samples, OST also plans to schedule analyses of plug samples as soon as practical after the plug samples are produced. CSRA will work with OST and its sampling contractor, Tetra Tech, to facilitate the scheduling. As a final step in this process, CSRA will collect data on the dates of preparation and analyses of each fillet plug and homogenized fillet tissue sample and calculate the total time that each sample was held before analysis (i.e., the time the samples are held in interim storage at the fish sample preparation laboratory before they are shipped to the analytical laboratory and in storage at the analytical laboratory before the laboratory initiates sample analysis).

B4. Analytical Methods

B4.1 Mercury

Fish tissue samples are being prepared and analyzed by ALS-Environmental (Kelso, WA), using Procedure I from "Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation" from Revision B of Method 1631 (1631B) for sample preparation (USEPA 2001b), and Revision E of Method 1631 (1631E) for the analysis of mercury in fish tissue samples (USEPA 2002). This method specifies using up to 1.5 g of tissue for the analysis. The sample is digested with a combination of nitric and sulfuric acids. The mercury in the sample is oxidized with bromine monochloride (BrCl) and analyzed by cold-vapor atomic fluorescence spectrometry.

To provide between 0.5 and 1.5 grams of tissue for analysis, each fillet plug sample will consist of two tissue plugs collected from the fish specimen. However, the actual mass of tissue will vary by fish species, size, and the depth of the tissue in the area sampled. For the purpose of this study, each fillet plug sample will consist of all of the tissue in the vial shipped to the laboratory. The entire mass in the sample vial is to be analyzed and the laboratory may not subsample or cut up the plugs to achieve a specific mass for analysis. Prior to analysis of each plug sample, the laboratory will weigh the entire mass of plug tissue provided in the sample vial and record the weight wet of the plug tissue.

Each ground fillet sample will consist of 5 to 10 grams of well-homogenized fillet tissue in a separate container. The laboratory will thaw each sample, stir the contents of the sample container with a clean utensil, remove approximately 1 gram of tissue for analysis, and record the wet weight of tissue analyzed.

Both fillet plug and homogenized fillet tissue sample results are reported based on the wet weight of the tissue sample, in nanograms per gram (ng/g). The mercury method detection limit (MDL) and minimum level (ML) provided by the analytical laboratory are 0.09 and 0.3 ng/g, respectively, based on a 1-g sample size.

B4.2 Selenium

Fish tissue samples are being prepared and analyzed by Brooks Applied Labs (Bothell, WA), using Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry Revision 5.4 (USEPA 1994), as modified by the laboratory to use a triple quadrapole mass spectrometer instead of a single quadrapole instrument. (This change, which is designed to reduce analytical interferences and improve sensitivity, has been reviewed by CSRA and is within the allowed flexibility for Clean Water Act methods at 40 CFR Part 136.6.) Prior to the ICP/MS analysis, the samples are being digested using an acid digestion procedure based on SW-846 Method 3050B (USEPA 1996).

The default size for solid sample described in Method 200.8 is 20 grams, which is far in excess of the mass of tissue in a typical 1- to 1.5-gram fish plug sample. As a result, the method detection limit (MDL) for selenium in the published method, and similar methods from other sources, is based on the 20-gram default sample size and does not reflect the method sensitivity that may be achieved for fish plug samples. Therefore, the analytical efforts of the laboratory in the selenium phase of this study will begin with two MDL studies for selenium: one using a

1-gram sample size and the second using a 5-g sample size. The results of both MDL studies will be submitted to CSRA and evaluated by CSRA and EPA before analyses of field samples begin.

Note: Because the MDL values are being developed as part of the overall effort, it is not possible to include them in this version of the QAPP (Revision 1) that is reviewed and approved before the selenium phase sample analyses begin. EPA will decide how to document the newly generated MDLs and any related information once they become available.

Each field-extracted and lab-extracted fillet plug sample consists of two tissue plugs collected from the fish specimen, which provides between 1 and 1.5 grams of tissue for analysis. However, the actual mass of tissue will vary by fish species, size, and the depth of the tissue in the area sampled. For the purpose of this study, each fillet plug sample consists of all of the tissue (both plugs) in the vial shipped to the laboratory. Prior to analysis of each plug sample, the laboratory will weigh the entire mass of plug tissue provided in the sample vial and record the wet weight of the plug tissue. The entire mass in the sample vial will be analyzed for selenium.

Each ground fillet sample shipped to the selenium analysis laboratory will consist of 20 to 25 grams of well-homogenized fillet tissue. The laboratory will thaw each sample, stir the contents of the sample container with a clean utensil, remove approximately 5 grams of tissue for analysis, and record the wet weight of tissue analyzed.

Both fillet plug and homogenized fillet tissue sample results will be reported based on the wet weight of the tissue sample, in nanograms per gram (ng/g). The percent solids data will be reported as a separate "analyte" and CSRA will use those data to compile the selenium results in both wet-weight and dry-weight formats for use in evaluation of the study results.

B4.3 Percent Solids

The laboratory will determine the percent solids content of each tissue sample in order to allow the results to be compared to the WQC in dry-weight format. For the plug samples, the laboratory will be provided with a second vial for each sample that contains a single plug and is labeled for solids analysis. For the homogenized fish tissue sample, the laboratory will use a 1-gram aliquot of the homogenized fish tissue from the single 20- to 25-gram ground fillet tissue aliquot container shipped to the laboratory.

Prior to analyzing each plug sample for percent solids, the laboratory will thaw the single plug sample and record the wet weight of plug tissue analyzed. The laboratory will thaw each ground tissue sample, stir the contents of the sample container with a clean utensil, remove approximately 1 gram of tissue for percent solids analysis, and record the wet weight of ground tissue analyzed.

The solids content of the samples will be determined by drying each percent solids sample to constant weight at 103 -105 °C, using Standard Method 2540G (APHA 2005).

B5. Analytical Quality Control

B5.1 Mercury

Quality control samples associated with each batch of tissue samples analyzed for mercury are summarized in Table 1 below. The cold-vapor atomic fluorescence instrument is calibrated daily, as described in Method 1631E and the laboratory's SOP. At least five calibration standards and a blank are used for calibration, and the variability in the calibration factors for the five standards must have a relative standard deviation (RSD) less than or equal to 15%. The calibration is verified after every 20 samples by the analysis of the ongoing precision and recovery (OPR) standard, or the laboratory control sample (LCS). The results for the OPR/LCS standard must fall within the limits in Table 1.

Due to the limited mass of each fillet plug sample, matrix spike/matrix spike duplicate (MS/MSD) pairs will not be analyzed for this study as called for in Method 1631E. Instead, the laboratory will analyze one matrix spike sample (MS) per batch of 20 homogenized fillet tissue samples and generate data for five replicates of each plug and homogenized fillet sample, which will provide more data on precision than a MS/MSD pair. The laboratory will also prepare and analyze an aliquot of an animal tissue-based reference material (e.g., a National Institute of Standards and Technology Standard Reference Material® or a Certified Reference Material from another recognized source) for each batch of 20 plug and homogenized fillet samples, which will provide sufficient data on bias.

Table 1. QC Samples and Acceptance Criteria for Mercury Analysis of Fish Tissue

QC Operation	Frequency*	Acceptance Limit	Corrective Action
Bubbler blank or System blank (depending on instrument configuration)	3 blanks run during calibration and with each analytical batch of up to 20 field samples	50 picograms (pg) of mercury	If the bubbler or system blank is above 50 pg, take corrective action to reduce the blank level to below 50 pg, and reanalyze any samples in the affected batch.
Method blank	3 method blanks per batch of up to 20 field samples, with analyses interspersed among the samples in the analysis batch	0.4 nanograms (ng) (400 pg) of mercury, *or* Less than one tenth the concentration of an associated sample	If any of the three method blank results is above 0.4 nanograms, • take corrective action to reduce the blank level to below 0.4 ng, • reanalyze any samples in the affected batch with results less than 10 times the observed results for any of the three blanks, and • flag sample results greater than 10 times the observed blank level to advise the data user of the potential contamination.
OPR/LCS	Prepared once per batch of up to 20 field samples, analyzed *once prior to* the analysis of any field samples, *and again at* the end of each analytical batch, spiked at 4.0 ng	70 - 130% recovery (5.6 –10.4 ng/g)	If the OPR recovery is not within the QC acceptance limits, • take corrective action and repeat the OPR analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.

Table 1. QC Samples and Acceptance Criteria for Mercury Analysis of Fish Tissue

QC Operation	Frequency*	Acceptance Limit	Corrective Action
Reference material sample	Once per batch of up to 20 plug samples and one per batch of 20 ground fillet samples	Per the provider of the reference material sample *or* 75 - 125% recovery if no criteria provided by the supplier	If the reference material sample results are not within the provider's acceptance limits, • take corrective action and repeat the reference material sample analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.
Matrix spike (MS) sample	Once per every 20 ground fillet tissue samples (**not** required for plug samples)	70 - 130% recovery	If the MS recovery is not within the QC acceptance limits, • take corrective action and repeat the MS analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.

* The term "field samples" refers collectively to field- and lab-extracted fillet plug samples and to homogenized fillet tissue samples provided to the analytical laboratory for mercury analysis.

B5.2 Selenium

Quality control samples associated with each batch of tissue samples analyzed for selenium are summarized in Table 2 below. The ICP-MS instrument is calibrated daily, as described in Method 200.8, Revision 5.4 and the laboratory's SOP. At least five calibration standards and a blank are used for calibration, and the variability in the calibration factors for the five standards must have a relative standard deviation (RSD) less than or equal to 15%. The calibration is verified after every 20 samples by the analysis of the ongoing precision and recovery (OPR) standard, or the laboratory control sample (LCS). The results for the OPR/LCS standard must fall within the limits in Table 2.

Due to the limited mass of each fillet plug sample, matrix spike/matrix spike duplicate (MS/MSD) pairs will not be analyzed for this study as called for in Method 200.8, Revision 5.4. Instead, the laboratory will prepare and analyze an aliquot of an animal tissue-based reference material (e.g., a NIST Standard Reference Material® or a Certified Reference Material from another recognized source) with each batch of 20 plug samples, which will provide sufficient data on bias.

The laboratory will analyze a second 5-g aliquot from one of the homogenized fillet tissue samples as a matrix spike sample for every batch of 20 homogenized fillet tissue samples.

Table 2. QC Samples and Acceptance Criteria for Selenium Analysis of Fish Tissue

QC Operation	Frequency*	Acceptance Limit	Corrective Action
Method blank	1 method blank per batch of up to 20 field samples	Less than the sample size-specific MDL determined for this study *or* Less than one tenth the concentration of an associated sample	If the method blank result is above the sample size-specific MDL, • take corrective action to reduce the blank level to below the MDL, • reanalyze any samples in the affected batch with results less than 10 times the observed results for the blank and • flag sample results greater than 10 times the observed blank level to advise the data user of the potential contamination.

Table 2. QC Samples and Acceptance Criteria for Selenium Analysis of Fish Tissue

QC Operation	Frequency*	Acceptance Limit	Corrective Action
OPR/LCS	Prepared once per batch of up to 20 field samples	80 - 120% recovery	If the OPR recovery is not within the QC acceptance limits, • take corrective action and repeat the OPR analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.
Reference material sample	Once per batch of up to 20 plug samples and one per batch of 20 ground fillet tissue samples	Per the provider of the reference material sample *or* 75 - 125% recovery if no criteria provided by the supplier	If the reference material sample results are not within the provider's acceptance limits, • take corrective action and repeat the reference material sample analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.
Matrix spike (MS) sample	Once per every 20 ground fillet tissue samples (**not** required for plug samples)	70 - 130% recovery	If the MS recovery is not within the QC acceptance limits, • take corrective action and repeat the MS analysis, beginning with a fresh aliquot, • reanalyze all samples in the affected analytical batch.

* The term "field samples" refers collectively to field-extracted and lab-extracted fillet plug samples and to homogenized fillet tissue samples provided to the analytical laboratory for selenium analysis.

B5.3 Percent Solids

There are no method-specified QC procedures associated with the percent solids determination.

B6. Instrument/Equipment Testing, Inspection, and Maintenance

All analytical instrumentation associated with the fish plug and fillet tissue sample analyses will be inspected and maintained as described in the respective analysis methods and laboratory SOPs.

B7. Instrument/Equipment Calibration and Frequency

The mercury analysis method for tissue samples, Method 1631E, specifies calibration with at least five calibration standards and multiple blanks, as described in Section B5.1 above.

Method 200.8, Revision 5.4, for selenium, specifies calibration with at least five calibration standards and multiple blanks, as described in Section B5.2 above.

The percent solids determination is based on a gravimetric procedure that involves calibration of the balance used to weigh the sample with a Class-S weight prior to each use.

B8. Inspection/Acceptance of Supplies and Consumables

The inspection and acceptance of any laboratory supplies and consumables associated with the mercury and selenium analyses are addressed in the laboratory operating procedures to be used,

and/or in each laboratory's existing overall quality system documentation. There are no additional requirements specific to this project, and therefore, none are described here.

B9. Non-direct Measurements

Non-direct measurements are not required for this project.

B10. Data Management

Data management practices employed in this study will be based on data management practices used for EPA's National Lake Fish Tissue Study and other OST fish contamination studies (e.g., the 2015 Great Lakes Human Health Fish Fillet Tissue Study). The data management (i.e., sample tracking, data tracking, data inspection, data quality assessment, database development) procedures have been regularly applied by CSRA to other technical studies. These procedures are being employed because they are effective, efficient, and have successfully withstood repeated internal and external audits, including internal review by EPA Quality Staff, public review and comment, judicial challenge, and the Government Accountability Office audit. These procedures, as implemented for the Fish Plug Evaluation Study, are summarized below.

Laboratory Data Management

Laboratory data management procedures include the following:

- The analytical laboratories are required to maintain all records and documentation associated with the analysis plug and fillet tissue samples for a minimum period of five years after completion of the study.
- To facilitate data tracking, each laboratory is required to use EPA-assigned sample numbers when reporting results.
- All results of field sample analyses and QC sample analyses must be reported in electronic format, as specified in the relevant analytical laboratory statement of work from CSRA.
- All required reports and documentation, including raw data, must be sequentially paginated and clearly labeled with the laboratory name and associated EPA sample numbers. Any electronic media submitted must be similarly labeled.
- Each laboratory will adhere to a comprehensive data management plan that is consistent with the principles set forth in EPA's Good Automated Laboratory Practices, (USEPA 1995). Those data management plans will be incorporated in their overall quality system documentation (e.g., their quality management plan).

CSRA Data Management

Data management procedures employed by CSRA include the use of 1) data review guidelines to promote consistency in data quality audits (data reviews) across reviewers and over time, 2) a multi-stage data review process designed to maximize the amount of useable data generated in each study, and 3) a database development process that facilitates rapid development of a database with at least 99.9% accuracy.

The data review guidelines facilitate rapid, consistent, accurate, and thorough data quality audits, and are based on those that were employed for the National Lake Fish Tissue Study (and subsequent OST fish contamination studies). These guidelines detail method-specific data review procedures for commonly used methods and more general procedures that can be applied to less frequently used methods. Where appropriate, CSRA will modify existing data review guidelines as necessary to reflect the methods, method modifications, and data quality objectives for the Fish Plug Evaluation Study and provide those modifications to all CSRA data review staff for implementation. Descriptions of any modifications will be retained in CSRA's project records.

Although each guideline is written for a specific method, technique, or group of analytes, all guidelines specify a general review process that ensure data are in proper format, are complete, are contractually compliant, and are usable. CSRA data review staff use this multi-stage process to verify the quality of each laboratory submission under the Fish Plug Evaluation Study. If an error is detected in any stage of the review, the CSRA data review staff and the CSRA Project Leader will initiate corrective action procedures to obtain the maximum amount of usable data from the study. These actions may serve to obtain missing data, correct typographical or transcription errors on data reporting forms, or initiate reanalysis of field or QC samples that do not meet the performance criteria for this study. Any such actions will be documented in CSRA's project records and reported to the EPA Project Manager.

Concurrent with the performance of data quality audits, CSRA staff will begin developing a Microsoft Access database of combined field and analytical results for field samples that were collected for and fillet tissue sample analytical results that were generated for the Fish Plug Evaluation Study. CSRA staff will develop an appropriate structure and organization for the Fish Plug Evaluation Study database. At a minimum, each record should include fields containing the following information:

- the EPA sample number
- lake or river name
- latitude/longitude where site is located
- sample collection date
- sample matrix (fillet tissue)
- sample type (field plug, lab plug, or homogenized fillet tissue)
- fish species (scientific and common names)
- fish specimen number
- length of fish specimen
- weight of fish specimen
- sample analysis date
- measured value for each target analyte (wet weight concentration)
- lipid measurement
- percent solids measurement
- percent moisture value derived from percent solids measurement
- dry weight concentration derived from selenium wet weight measurement and percent solids measurement

The Access database will contain the field and analytical results from all the Fish Plug Evaluation Study samples, including the whole fish and plug sample collection information and

analytical and QC results for analyses of the fillet tissue samples for mercury, selenium, percent solids, and lipids. As noted above, it will also include derived values for percent moisture and for selenium dry weight concentrations. The mercury results in the database will optimally include data for 60 whole fish samples, 300 field-extracted fillet plug samples, 300 lab-extracted fillet plug samples and 300 homogenized fillet tissue samples before the complete mercury data set is transmitted to EPA. The selenium results in the database will optimally include data for 30 whole fish samples, 120 field-extracted fillet plug samples, 120 lab-extracted plugs, and 120 homogenized fillet tissue samples before the complete selenium data set is transmitted to EPA. The database will also contain data for the QC samples associated with each analytical batch of the fillet tissue samples as described in Section B5. The structure of the database will allow CSRA to segregate these QC results from the fillet tissue sample analytical results.

As with the data quality audits, CSRA uses a multi-stage process of inspections and corrective actions to facilitate timely, efficient construction of a database that is at least 99.9% accurate. The database development process begins with a completeness check to verify the laboratory has submitted data on an electronic medium that contains all data in an appropriate format. If deficiencies are found, CSRA will initiate appropriate corrective action measures.

The CSRA data review staff responsible for performing the data quality audit verify that the electronic data accurately reflect the hard copy submission. Accuracy is confirmed by spot checking at least 10% of all results that were downloaded directly from an analytical instrument in the laboratory and by performing a 100% QC check of data that were manually entered by the laboratory or CSRA. Corrective actions are taken as needed to resolve deficiencies. Following completion of the data quality review, the CSRA data reviewer and the CSRA Project Leader modify the database to reflect data usability determinations. A report, generated to reflect the modified database, is then reviewed by the CSRA data review staff to verify database accuracy before submission to EPA. These reports are maintained in CSRA's project files.

C. ASSESSMENT AND OVERSIGHT

C1. Assessments and Response Actions

The laboratory contracts prepared to support this study stipulate that the laboratories have a comprehensive QA program in place and operating at all times during the performance of their contract, and that in performing laboratory work for this study, the laboratories shall adhere to the requirements of their QA programs (ALS-Environmental 2014 and Brooks Applied Labs 2017). These materials were reviewed by CSRA during the solicitations for mercury analysis and selenium analysis, as part of an assessment of laboratory capabilities. A copy of the QA plans are maintained on file at CSRA and will be made available to EPA for review on request.

Sections C1.1 through C1.6 describe other types of assessment activities and corresponding response actions identified to ensure that data gathering activities in the Fish Plug Evaluation Study are conducted as prescribed and that the performance criteria defined for the study are met.

C1.1 Surveillance

The CSRA Project Leader schedules and tracks all analytical work performed by the laboratories designated for mercury and selenium analyses. The Project Leader coordinates with staff at the

sample preparation laboratory regarding fish tissue sample shipments to the respective analytical laboratories.

When samples are shipped to the analytical laboratory for mercury or selenium analysis, the CSRA Project Leader contacts designated laboratory staff by email to notify them of the forthcoming shipment(s) and requests that they contact CSRA on the scheduled day of delivery if the shipments do not arrive intact. Within 24 hours of scheduled sample receipt, CSRA contacts the laboratories to verify that the samples arrived in good condition, and if problems are noted, works with the laboratories and EPA to resolve the problems as quickly as possible to minimize data integrity problems.

The laboratory designated for mercury analysis of Fish Plug Evaluation Study fillet tissue samples is permitted to work two batches ahead of the CSRA/EPA review of the QC results associated with the fillet tissue sample analyses. CSRA will immediately notify the EPA Project Manager of any mercury laboratory delays that are anticipated to impact EPA schedules.

The laboratory designated for selenium analysis of Fish Plug Evaluation Study fillet tissue samples is permitted to work three batches ahead of the CSRA/EPA review of the QC results associated with the fillet tissue sample analyses. CSRA will immediately notify the EPA Project Manager of any selenium laboratory delays that are anticipated to impact EPA schedules.

Finally, the CSRA Project Leader monitors the progress of the data quality audits (data reviews) and database development to ensure that the laboratory data submission is reviewed in a timely manner. In the event that dedicated staff are not able to meet EPA schedules, CSRA will identify additional staff who are qualified and capable of reviewing the data in a timely manner. If such resources cannot be identified, and if training new employees is not feasible, CSRA will meet with the EPA Project Manager to discuss an appropriate solution.

C1.2 Product Review

Product reviews for validated analytical data packages are performed within CSRA to verify that the CSRA data reviews are being performed consistently over time and across data reviewers, that the review findings are technically correct, and that the reviews are being performed in accordance with this QAPP. Product reviewers are charged with evaluating the completeness of the original CSRA data review, the technical accuracy of the reviewer's findings, and the technical accuracy of the analytical database developed to store results associated with the data package. Product reviews are conducted on at least 10% of the data packages. Qualified product reviewers include any staff members that have been trained in CSRA data review procedures, are experienced in reviewing data similar to those being reviewed, and are familiar with the requirements of this QAPP. To ensure the findings of each data review are documented in a consistent and technically accurate manner, CSRA staff review 100% of the data qualifier flags entered into the project database.

The Fish Plug Evaluation Study data files prepared by CSRA for statistical analysis of the data are reviewed internally by CSRA staff and independently by the EPA Project Manager with support from Tetra Tech.

C1.3 Quality Systems Audit

A quality system audit (QSA) is used to verify, by examination and evaluations of objective evidence, that applicable elements of the quality system are appropriate and have been developed, documented, and effectively implemented in accordance and in conjunction with specified requirements. The focus of these assessments is on the quality system processes – not on evaluating the quality of specific products or judging the quality of environmental data or the performance of personnel or programs. The SHPD QA Coordinator may perform a QSA of the Fish Plug Evaluation Study mercury analyses.

C1.4 Readiness Review

Readiness reviews of the capabilities of the mercury and selenium analysis laboratories to produce acceptable sample results begin with a review of materials submitted by the laboratories during the solicitation process and continue during a kick-off conference call with each of the laboratories (ALS-Environmental [mercury] and Brooks Applied Labs [selenium]). The requested materials include information about each laboratory's capacity, past experience with tissue analyses, and accreditations or certifications for mercury or selenium analyses in tissue and other matrices. These materials are reviewed during the solicitation process to assess the competency of each laboratory and are kept on file by CSRA.

Readiness reviews are performed by CSRA data reviewers. If problems are identified during these reviews, CSRA staff work with the applicable laboratory, to the extent possible, to resolve the problem prior to awarding an analysis contract. If the problem cannot be resolved within the time frame required by EPA, the CSRA Project Leader notifies the EPA Project Manager immediately. Records of these reviews and any corrective actions are maintained by CSRA separate from the analytical results for the field samples. CSRA staff will document their findings and recommendations concerning the readiness review as part of a written analytical QA report to EPA.

C1.5 Technical Systems Audit

Each of the laboratory contracts require that the laboratory be prepared for and willing to undergo an on-site, or technical systems, audit of its facilities, equipment, staff, sample processing, tissue sample analysis, training, record keeping, data validation, data management, and data reporting procedures. An audit will be conducted only if the results of the readiness reviews, data quality audits, and surveillance suggest serious or chronic laboratory problems that warrant on-site examinations and discussion with laboratory personnel.

If such an audit is determined to be necessary, a standardized audit checklist may be used to facilitate an audit walkthrough and document audit findings. Audit participants may include the EPA Project Manager and/or the SHPD QA Coordinator (or a qualified EPA staff member designated by the OST QA Officer) and a CSRA staff member experienced in conducting laboratory audits. One audit team member will be responsible for leading the audit and conducting a post-audit debriefing to convey significant findings to laboratory staff at the conclusion of the audit. Another audit team member will be responsible for gathering pre-audit documentation of problems that necessitated the audit, customizing the audit checklist as necessary to ensure that those problems are addressed during the audit, documenting audit

findings on the audit checklist during the audit, and drafting a formal report of audit findings for review by EPA.

C1.6 Data Quality Assessment

Upon completion of data verification and validation procedures (see Section D1), CSRA staff will create an analytical database that contains all fillet tissue and QC sample results from the Fish Plug Evaluation Study (see Section B10). At selected intervals and upon completion of the study, the CSRA Project Leader will perform analyses to verify the accuracy of the database. The procedures are directed at evaluating the overall quality of the database against data quality objectives established for the study and in identifying trends in fillet tissue sample results derived from field samples and QC results obtained during the study. CSRA staff will document their findings and recommendations concerning this data quality assessment and provide them to EPA.

C2. Reports to Management

CSRA tracks the receipt of data submissions for the plug and homogenized fillet tissue analyses and advises the EPA Project Manager of progress on a monthly basis.

Following data verification and validation of all project analytical data, CSRA applies data qualifier flags, where needed, to the fish tissue results in the project database that describe data quality limitations and recommendations concerning data use. The data qualifier flags are based on those developed for the National Lake Fish Tissue Study and the complete list of qualifier flags used and their implications for data use will be summarized in a report to EPA at or near the end of the data assessment process.

The CSRA Project Leader provides a monthly report to the EPA Project Manager that describes the status of all current analysis and data review activities, during each month in which analyses and data review are conducted.

D. DATA VALIDATION AND USABILITY

This QAPP addresses the generation of data from fish fillet plug and homogenized fillet tissue samples. Sections D1, D2, and D3 of this QAPP apply to all of the analytical data generation for the Fish Plug Evaluation Study.

D1. Data Review, Verification, and Validation

The data review, verification, and validation aspects of the fish plug and homogenized fillet tissue analysis are described below for all of the analytical data generated for the Fish Plug Evaluation Study.

D1.1 Data Review

All laboratory results and calculations are reviewed by the Laboratory Manager prior to data submission. Any errors identified during this peer review are returned to the analyst for correction prior to submission of the data package. Following correction of the errors, the Laboratory Manager verifies that the final package is complete and compliant with the contract,

and signs each data submission to certify that the package was reviewed and determined to be in compliance with the terms and conditions of the contract.

D1.2 Data Verification

The basic goal of data verification is to ensure that project participants know what data were produced, if they are complete, if they are contractually compliant, and the extent to which they meet the objectives of the study. Every laboratory data package submitted under this study is subjected to data verification by qualified CSRA staff who have been trained in procedures for verifying data and who are familiar with the laboratory methods used to analyze the samples. This includes all of the mercury, selenium, and percent solids data generated under this QAPP and any subsequent QAPP revisions. The verification process is designed to identify and correct data deficiencies as early as possible in order to maximize the amount of usable data generated during this study. The CSRA Project Leader verifies the summary level results for these analytical data, determines if they meet the project objectives in this QAPP, and reports the verification findings to OST.

D1.3 Data Validation

Data validation is the process of evaluating the quality of the results relative to their intended use. Data need not be "perfect" to be usable for a particular project, and the validation process is designed to identify data quality issues uncovered during the verification process that may affect the intended use. One goal of validation is to answer the "So what?" question with regard to any data quality issues. CSRA data review staff will validate all of the mercury, selenium, and percent solids analysis results to be generated under this QAPP and any subsequent QAPP revisions.

D2. Verification and Validation Methods

D2.1 Verification Methods

In the first stage of the data verification process, CSRA data review chemists perform a "Data Completeness Check" in which all elements in each laboratory submission are evaluated to verify that results for all specified samples are provided, that data are reported in the correct format, and that all relevant information, such as preparation and analysis logs, are included in the data package. Corrective action procedures will be initiated if deficiencies are noted.

The second stage of the verification process focuses on an "Instrument Performance Check" in which the CSRA data review chemists verify that calibrations, calibration verifications, standards, and calibration blanks were analyzed at the appropriate frequency and met method or study performance specifications. If errors are noted at this stage, corrective action procedures will be initiated immediately.

Stage three of the verification process focuses on a "Laboratory Performance Check" in which CSRA data review chemists verify that the laboratory correctly performed the required analytical procedures and was able to demonstrate a high level of precision and accuracy. This stage includes evaluation of QC elements such as the laboratory control samples, method blanks, matrix spike samples and/or reference samples, where applicable. Corrective action procedures will be initiated with the laboratories to resolve any deficiencies identified.

In stage four of the verification process, the CSRA data review chemist performs a "Method/Matrix Performance Check" to discern whether any QC failures are a result of laboratory performance or difficulties with the method or sample matrix. Data evaluated in this stage may include matrix spike and reference sample results. The CSRA data review chemist also verifies that proper sample dilutions were performed and that necessary sample cleanup steps were taken. If problems are encountered, the CSRA data review chemist will immediately implement corrective actions.

D2.2 Validation Methods

CSRA data review chemists perform a data quality and usability assessment in which the overall quality of data is evaluated against the performance criteria (see Section B5 for a description of performance criteria). This assessment strives to maximize use of data gathered in this study based on performance criteria established for this study. This is accomplished by evaluating the overall quality of a particular data set rather than focusing on individual QC failures. Results of this assessment will be documented in a project QA report developed after all of the results have been evaluated, and before they are used in any final decision making.

During this assessment, data qualifier flags are applied to the project results to identify any results that did not meet the method- or project-specific requirements; CSRA data review chemists still may also apply additional qualifiers that indicate an assessment of the impact of the problem. For example, individual sample results are often qualified based on the presence of the analyte in a method blank associated with samples prepared together (e.g., extracted or digested in the same batch). While it is important to identify any result associated with the presence of the analyte in the blank, the relative significance of the potential for sample contamination is assessed using commonly accepted "rules." In instances where the amount of the analyte found in the method blank has very limited potential to affect the field sample result, an additional data qualifier is applied to that field sample result to indicate that the result was not affected by the observed blank contamination. Similar assessments made for other data quality concerns may result in the application of additional flags that reconcile the observed data quality concerns with the user requirements and warn the end user of any limitations to the results (i.e., potential low or high bias, blank contamination, etc.). All of the data qualifiers are included in the data file along with summary level comments that explain the implication in relatively plain English.

Where data quality concerns suggest that no valid result was produced for a given analyte, the result for the analyte is flagged for exclusion in the database, and the comments provide the rationale for the exclusion. The final report of study results generated from the database and provided to EPA will not include such invalid results, although the records marked for exclusion will be retained in the database for transparency. As noted earlier, the overall verification and validation process is designed to maximize the amount of usable data for the project, and flagging results for exclusion in the final database is intended as a last resort.

D3. Reconciliation with User Requirements

The QC results for the analyses of the fish plug and homogenized fillet tissue samples for mercury and selenium are assessed against the QC acceptance criteria for those respective analyses. The CSRA Project Leader tracks laboratory performance, notifies the EPA Project Manager of any issues, initiates corrective actions, and tracks progress by each sample analysis laboratory.

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